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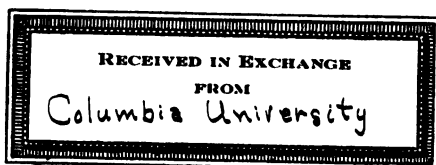
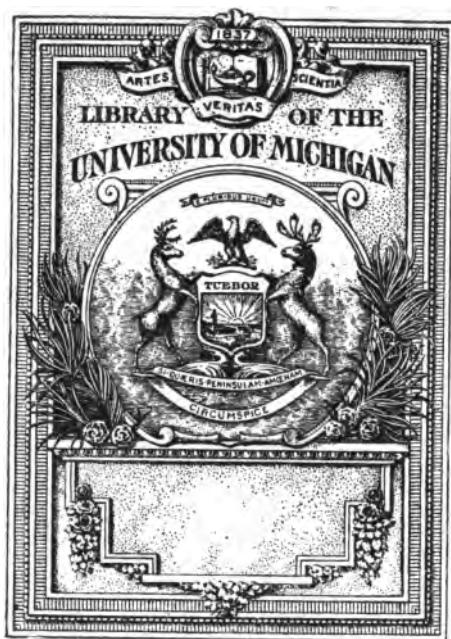
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**The Hydration of Normal Sodium Pyrophosphate
to Orthophosphate in Varying Concentrations
of Hydrogen Ion at Forty-five Degrees
Centigrade.**

DISSERTATION

Submitted in Partial Fulfillment of the requirements
for the Degree of Doctor of Philosophy in
the Faculty of Pure Science of
Columbia University.

BY

WALDEMAR C. HANSEN, B. S.

NEW YORK CITY

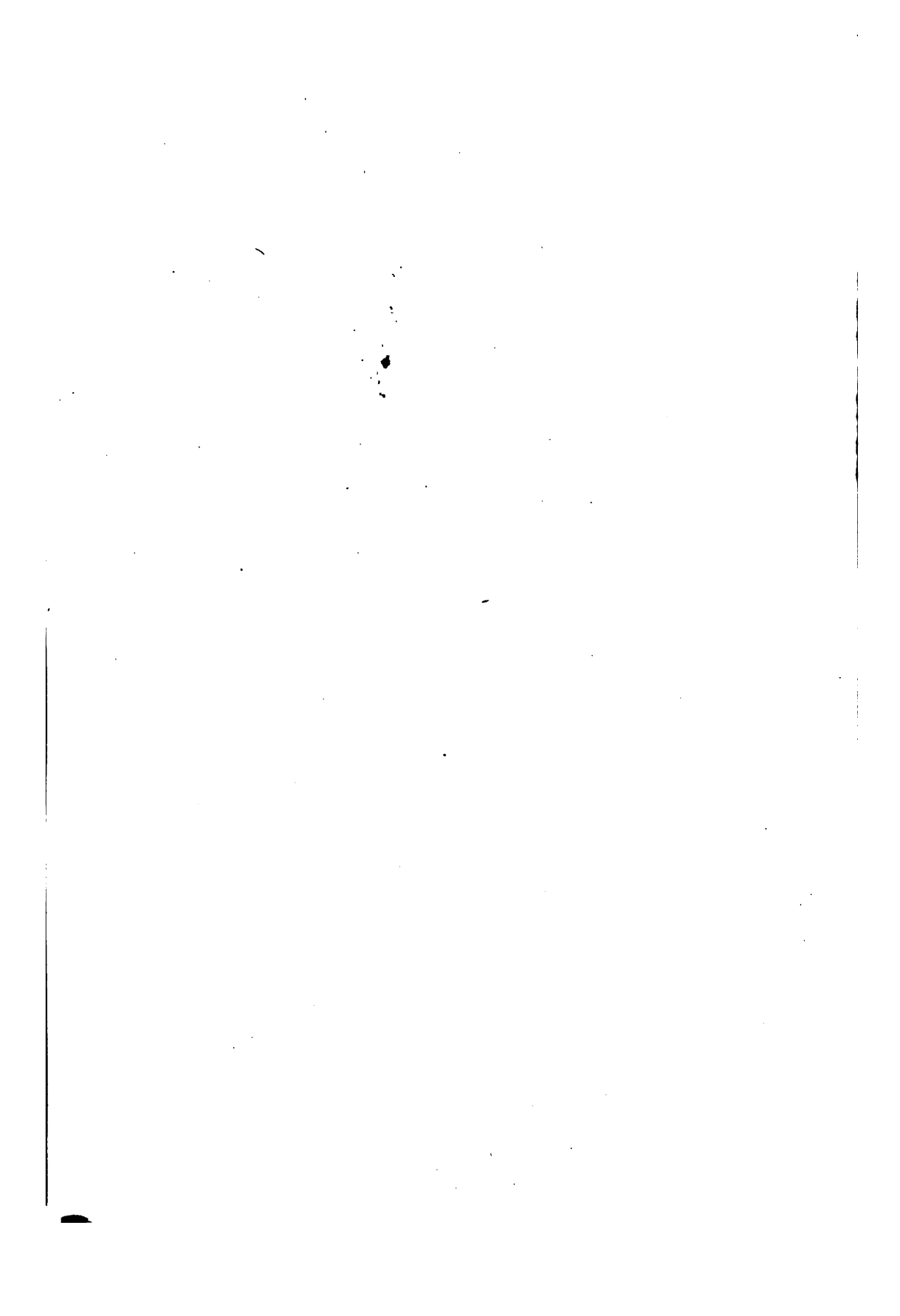
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ACKNOWLEDGMENT

The following investigation was undertaken at the suggestion of Professor Samuel J. Kiehl and carried out under his direction. It gives me pleasure to express my thanks and appreciation for his constant advice and assistance received throughout the investigation.

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The Hydration of Normal Sodium Pyrophosphate to Orthophosphate in Varying Concentrations of Hydrogen Ion at 45° Centigrade.

Since the work of Graham¹ on the phosphoric acids the problem of the hydration of pyrophosphoric acid has been of interest. A part of the interest was due to the difference of opinion among chemists as to whether the hydration of metaphosphoric acid was direct to orthophosphoric acid or whether pyrophosphoric acid was formed as an intermediate product^{1, 2, 3, 4, 5, 6, 7}. Beans and Kiehl⁸ showed that pyrophosphate is formed as an intermediate product in the hydration of sodium monometaphosphate to orthophosphate. Therefore to understand more fully the hydration of sodium monometaphosphate to orthophosphate it seems advisable to study the hydration of a pyrophosphate to orthophosphate under the same conditions.

One difficulty encountered by previous workers on this problem was due to the lack of a suitable method for the determination of the amounts of the different phosphates present when present together. In order to study the reaction it is necessary to have a method of determining the amounts of each of the phosphates present at any given time.

The first to study this problem were André and Berthelot⁵. They used a method of acidimetry to determine the amounts of each of the acids present at any definite time. They discarded this method and attempted⁵ to develop a gravimetric separation. In this separation they precipitated a magnesium ammonium pyrophosphate of indefinite composition by heating the solution to be analyzed, acidified with acetic acid, for three or four hours on a boiling water bath. Since temperature⁹ and hydrogen ion^{5, 9} both have a marked effect on the rate of hydration this method could not be applicable for a quantitative study of this hydration.

No one attempted a further study of this problem until 1909 when Abbott⁹ studied it by conductivity measurements. In his method he measured the conductivity of aqueous solu-

tions of pyrophosphoric acid of varying concentrations and at different temperatures. The time at which the conductivity of a given solution became constant he considered as the time required for the complete hydration. He determined the amounts hydrated at different intervals during the reaction by measuring the conductivity of mixtures of pyrophosphoric acid and orthophosphoric acid corresponding in composition to certain percentages of hydration of an original pyrophosphoric acid solution. He plotted these conductivity values against composition and got straight line curves. So by measuring the conductivity of his hydration solution and referring to the curves he could determine the percentage hydrated at that time.

These three studies are the only ones which have been made heretofore in which the reaction has been followed throughout its entire course. Since the method⁵ of André and Berthelot was not applicable to the problem in question, and since Abbott's investigations were at temperatures where the reaction was complete in a few hours and on a few concentrations of pyrophosphoric acid only, thus limiting the concentration of hydrogen ion to that furnished by the acid, neither investigation has furnished sufficient information regarding the hydration of a pyrophosphate as compared with the hydration of a metaphosphate as previously pointed out⁶. Therefore this problem was undertaken to study the hydration of a pyrophosphate to the orthophosphate in varying concentrations of hydrogen ion and at constant temperature. With this in view, materials have been prepared and methods developed whereby the factors and conditions influencing the reaction could be controlled and studied to completion. An account of this investigation will be presented under the following headings Apparatus, Preparation of Materials, Method of Procedure, Experimental Data, Discussion, and Summary.

APPARTUS

Thermostat: A Freas sensitive thermostat was used to maintain a constant temperature for the entire work of hydration and hydrogen ion concentration measurement. By it a constant temperature of $45^{\circ}\text{C.} \pm .01$ was secured.

Potentiometer: Measurements for the determination of the concentration of hydrogen ion were made with a Leeds and Northrup direct-reading potentiometer of low resistance.

Galvanometer: In connection with the potentiometer a Leeds and Northrup, type R, D'Arsonval galvanometer equipped with a telescope and scale was employed. Its resistance was 510 ohms, its sensibility 309 megohms. The period was 2.7 seconds, and the critical damping resistance was 1800 ohms.

Standard Cell: A model 4, No. 4208 Weston standard cell served as a basis for all electrical measurements. Its value was 1.01872 volts at 22° C. This voltage was checked against a cell whose value was checked against a Bureau of Standards standard.

Calomel and Hydrogen Cells and Electrodes: The calomel and hydrogen cells and electrodes employed in the measurement of hydrogen ion concentration were of the type described in the article of Fales and Vosburgh¹⁰ excepting a modification of the hydrogen cell by a stop cock on the arm leading to the salt bridge.

Crucible Furnace: The amount of water of hydration and of constitution of the di-sodium orthophosphate and the amount of water of hydration of the normal sodium pyrophosphate was determined by heating the salts in an electric resistance furnace. It was calibrated for temperature by a thermocouple in such a way that its temperature could be controlled by measurement of the current with an accuracy of $\pm 10^\circ$ C.

PREPARATION OF MATERIALS

Normal Sodium Pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$): The purest Normal Sodium Pyrophosphate obtainable was recrystallized three times from distilled water. The solution of the pyrophosphate was cooled in ice water and stirred continuously until the crystallization was complete; this gave a very uniform crystalline product. The crystals were washed three times with distilled water on a Buchner funnel with suc-

tion. They were then spread out on a glass surface and allowed to dry for about twelve hours at room temperature. They were then finely pulverized in an agate mortar and stored in a glass-stoppered bottle.

This normal sodium pyrophosphate was analyzed for water of hydration by weighing a sample into a platinum crucible and heating in the electric crucible furnace previously described. The temperature was gradually raised to 450° C. during the first hour by increasing the current. It was kept at that temperature for two hours and then weighed; reheating for an hour caused no change in weight. The following table gives the analysis of the normal sodium pyrophosphate used in this research:

Lot I,	Water of Hydration	Average
Sample 1	40.45%	40.45%
Sample 2	40.44%	
Sample 3	40.46%	
Lot II,		
Sample 1	40.45%	40.45%
Sample 2	40.45%	

The theoretical value for water of hydration of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ is 40.36%.

It was then analyzed for phosphorus content. The phosphorus content was calculated on the basis that the material was $\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{XH}_2\text{O}$ where $\text{XH}_2\text{O} = 40.45\%$. The percentage of phosphorus as calculated should be 13.89%. This was checked by converting weighed samples to orthophosphate by boiling with six molar hydrochloric acid for from four to five hours. The orthophosphate was then determined by the standard magnesium mixture method. The following table gives the results of these analyses:

Lot I.	$\text{Na}_4\text{P}_2\text{O}_7 \cdot \text{XH}_2\text{O}$	P calc. on	P determined
Sample	Taken	basis of 13.89%	as ortho.
1.....	.3269 gms.	.0454 gms.	.0458
2.....	.4084	.0568	.0568
3.....	.3971	.0552	.0556
4.....	.4448	.0618	.0622

The calculated and determined values for percentage of phosphorus in the material check within experimental error and therefore the value of 13.89 per cent. phosphorus was used in making up all solutions for hydrations.

Di-Sodium Orthophosphate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$): Di-Sodium orthophosphate was prepared by crystallizing three times from distilled water by the addition of an equal volume of redistilled 95% alcohol and cooling in ice water. The solution was stirred constantly until the crystallization was complete. In this way a very uniform crystalline product was secured. Di-sodium orthophosphate is similar to mono-sodium orthophosphate⁸ forming two liquid phases upon the addition of the alcohol, and crystallization taking place first at the juncture of the two liquid phases. As crystallization proceeds the upper phase disappears, leaving but one phase at complete precipitation. The crystals were filtered on a Buchner funnel with suction and washed three times with alcohol. They were dried by spreading out on a glass surface for about an hour at room temperature; at the end of that time they were finely pulverized in an agate mortar and put in a glass-stoppered bottle. Di-sodium orthophosphate crystallizes as $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ which gradually decomposes forming lower hydrates when exposed to the air. It was, therefore, decided not to attempt to prepare a constant hydrate, but to dry sufficiently to remove all possibility of free moisture and then analyze that material for water of constitution and water of hydration. The analyses for water content were made by weighing a sample of the material into a platinum crucible and heating in the electric furnace previously described until constant weight was obtained. The material was heated gradually for one hour at first, then the rheostat was set for a temperature of 450°C . and held there for two hours. In this way constant results were obtained by $\text{Na}_2\text{HPO}_4 \cdot \text{XH}_2\text{O}$ being converted to $\text{Na}_4\text{P}_2\text{O}_7$, and the loss of weight was the total water content of the salt, that of hydration and constitution.

Lot I.

Sample	% water of constitution and hydration	Mean	Calculated % of phosphorus in the material
1.....	51.48	51.48	11.32
2.....	51.48		

Lot II.

Sample	% water of constitution and hydration	Mean	Calculated % of phosphorus in the material
1.....	51.91	51.98	11.19
2.....	52.06		

Lot III.

Sample	% water of constitution and hydration	Mean	Calculated % of phosphorus in the material
1.....	56.51	56.51	10.14
2.....	56.52		

Hydrochloric Acid: The hydrochloric acid used was prepared by distilling a constant boiling solution through a quartz condenser. The first and last portions were rejected.

Potassium Chloride: The calomel cells and salt bridges were prepared from potassium chloride which was purified by re-crystallization three times from distilled water and then fused in platinum.

Mercurous Chloride: The mercurous chloride employed to make calomel cells for hydrogen ion concentration measurements was prepared by the electrolytic method of Ellis¹¹, from mercury re-distilled according to Hulett¹² and hydrochloric acid prepared as described above.

Magnesium Mixture: The magnesium mixture was prepared by dissolving 320 grams of magnesium chloride hexahydrate, 225 grams of ammonium chloride, and 250 c.c. of 15 M. ammonium hydroxide (specific gravity .9) in 2250 c.c. of water.

Magnesium Chloride Solution: The magnesium chloride solution used was made by dissolving 110 grams magnesium chloride hexahydrate in 50 c.c. of water, which gave approximately a volume of 130 c.c. of solution.

METHOD OF PROCEDURE

In planning a method of procedure the first considerations were the factors influencing the reaction and they have as far as possible been either measured or controlled as in the work of Beans and Kiehl in the hydration of sodium monometa-phosphate. The temperature, the concentration of hydrogen ion, the concentration of orthophosphate and the concentration of pyrophosphate are the variable factors which influence the hydration of normal sodium pyrophosphate.

The temperature was regulated and controlled at $45^{\circ}\text{C} \pm .01$. The concentration of hydrogen ion was measured at intervals during the hydration. The amount of pyrophosphate changed to orthophosphate was determined at intervals by hydrogen ion concentration measurements; this was also checked over the last fifty per cent. of the hydration by gravimetric analysis.

Preparation of Solutions:

All solutions made up for hydration were prepared at 20°C . The finely pulverized normal sodium pyrophosphate was weighed and transferred to a 1,000 c.c. volumetric flask. Distilled water was added leaving sufficient room for the hydrochloric acid required to furnish the hydrogen ion concentration wanted in that solution. The acid used was the constant boiling mixture previously described. The value of the acid was determined by measuring out 30 c.c. portions by means of a burette and building them up to 1,000 c.c. at 20°C . These acid solutions were titrated with standard sodium hydroxide solution. The value of the sodium hydroxide solution was determined by titration against Bureau of Standards benzoic acid. Phenolphthalein was used as indicator in all the titrations. As the acid was added the flask was rotated so as to avoid acquiring a greater hydrogen ion concentration in any portion of the solution than that ultimately desired. The solution was then brought quickly to 20°C ., and the flask filled to the graduation, then mixed thoroughly and put in a "non sol" bottle and placed in the thermostat. The whole operation beginning with the addition of the acid required not more than ten minutes. The specific gravity of the solution was taken

at 20° C. by means of the Westphal balance calibrated at 20° C., at the beginning of the hydration, again at about fifty per cent., and finally at complete hydration. These specific gravity values are given in the tables for each solution. There was no change in volume in any of the solutions during hydration (except D₁ and D₂ see Table 2) greater than one part in a thousand, the precision of the balance. This was further checked by measuring the specific gravity of three of the solutions at the beginning and at the end of the reaction, by means of a pycnometer. The change was not greater than one part in a thousand so that the Westphal balance was sufficiently accurate. The concentrations of all of the solutions were calculated in moles per liter at 20° C. so by knowing the specific gravity at 20° C. the concentration of the phosphates in any weighed quantity of the solution could be calculated.

The change of specific gravity of D₁ and D₂ was two parts in a thousand. Since they are the only ones that show this change it is believed to be due to some other cause than the change in volume due to hydration. The final hydrogen ion concentrations of these solutions were also higher than expected from the final value obtained for the analytical curve; all the other solutions approached quite closely in final hydrogen ion concentrations that determined for the analytical curves. So it seems quite possible that some evaporation must have taken place in solutions D₁ and D₂, thus making them more concentrated. This would explain both the specific gravity change and the higher hydrogen ion concentration. All solutions were handled so as to minimize evaporation as much as possible because at 45° C. and for the long times that the solutions were being run evaporation would become quite appreciable unless every precaution was taken to guard against it.

Measurement of Concentration of Hydrogen Ion.

All hydrogen ion measurements were made at 45° C. by The Saturated Potassium Chloride Calomel Cell method developed in this department¹³. Samples of the solution in process of hydration were taken by means of a pipette and introduced into the hydrogen cell previously rinsed three times

with the solution being measured. The voltage was measured after ten minutes and again after twenty minutes which was the time required for equilibrium. The hydrogen was purified by passing it successively through alkaline permanganate, mercuric chloride, alkaline pyrogallol, cotton, and a portion of the same solution to be measured placed in the thermostat.

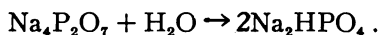
The calculation of the molar concentration of hydrogen ion was made by means of the formula

$$\log C_{H^+} = \frac{A - E}{DT}$$

In this formula C_{H^+} is the concentration of hydrogen ion, E the observed voltage, T the absolute temperature, D a constant whose value is .000198, and A a constant whose value is .2342 for forty-five degrees centigrade.

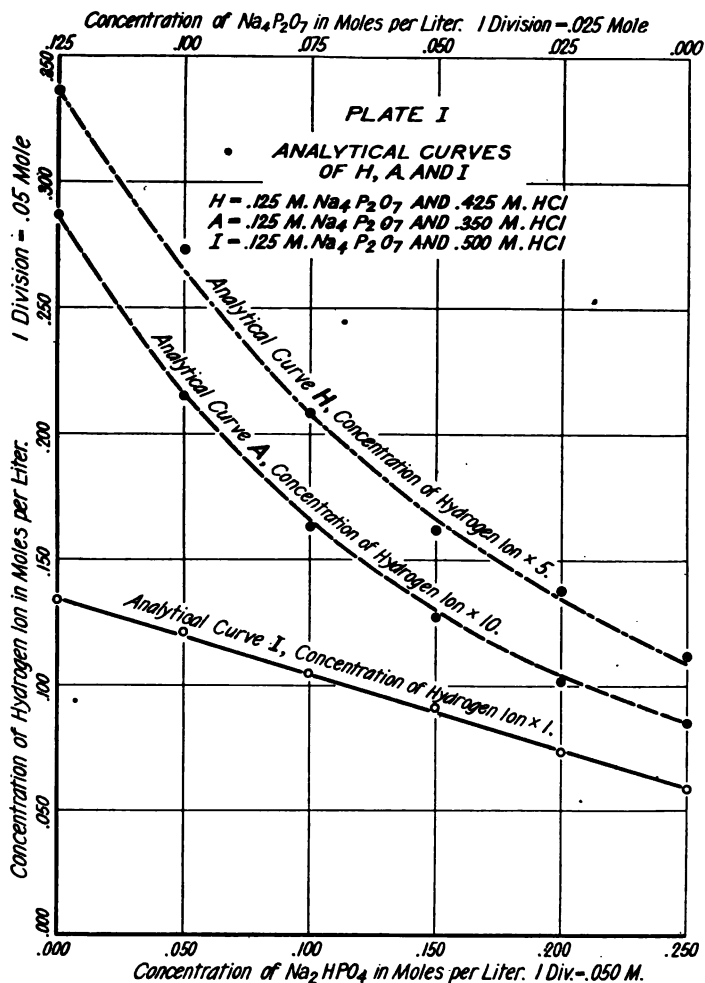
Determination of the Percentage of Hydration by Hydrogen Ion Concentration Measurements.

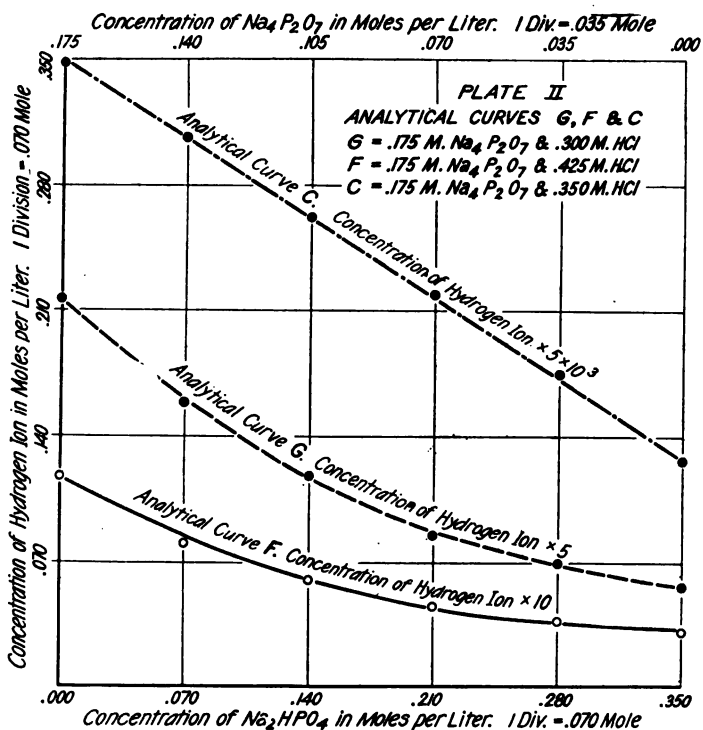
It is well known that the hydration of normal sodium pyrophosphate is represented by the following equation:



The method used in making the initial solutions for the hydrations studied was to make up a solution of normal sodium pyrophosphate of a certain concentration containing hydrochloric acid of a certain concentration. It was therefore possible to make up solutions containing pyrophosphate, orthophosphate and hydrochloric acid identical in composition with any sample of the particular solution in the process of hydration, provided the specific gravity change during hydration was within the precision of experimental measurements. It has been pointed out previously that the specific gravity change was not greater than one part in a thousand which is within the required accuracy. Therefore, it was possible to make up analytical curves by which the hydration could be followed by hydrogen ion concentration measurements. These curves were made up by preparing six solutions which corresponded in composition to the initial solution being studied and to each twenty per cent. hydration, the final solution

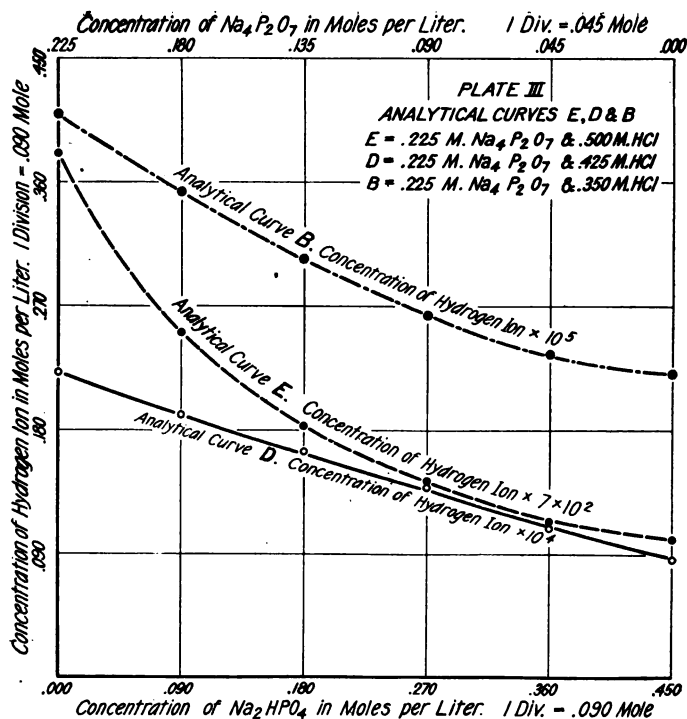
corresponding to complete hydration. The molar hydrogen ion concentration measured on each of these six solutions was plotted against molar concentration of orthophosphate. This gave a curve from which, by knowing the concentration of hydrogen ion in any particular solution being hydrated, the composition of that solution could be determined from the curve. The data for these curves are given in Tables 3, 4, 5, 6, 7, 8, 9, 10, and 11. The curves are given in plates I, II, and III.





The materials used in preparing these solutions were the same as used in preparing the hydration solutions with the addition of the di-sodium orthophosphate which is described under preparation of materials. The method of preparing these solutions was to make up 100 c.c. in exactly the same way as described under preparation of solutions. The hydrogen ion concentration was measured immediately in the same way as described under measurement of hydrogen ion concentration. The entire time from the addition of the acid until the final hydrogen ion concentration was measured was never over thirty minutes, which introduced very little error into these measurements due to hydration during the time of measuring corroborated by actual work of hydration.

These analytical curves were plotted on a scale such that the concentration of orthophosphate could be read to two-



tenths of one per cent. In every analytical curve the slope was steep enough over the larger part that a change of two-tenths of a millivolt (the precision of potentiometer readings) in hydrogen ion concentration measurements gave an error in composition of less than one per cent., and at the extreme end where the slope became less steep the error was less than two per cent., so that the composition could be determined by hydrogen ion concentration measurements with an accuracy of less than two per cent. over the entire curve.

Separation of Ortho and Pyrophosphate.

The values for percentages of hydration as determined by hydrogen ion concentration measurements were checked over the last fifty per cent. by gravimetric separation. As pointed out in the introduction, no satisfactory gravimetric separation for ortho and pyrophosphate was known. It was known¹⁴

however, that pyrophosphate of magnesium was soluble in magnesium salts. A decision was therefore made to attempt a separation by use of magnesium chloride and magnesium mixture. A number of qualitative determinations were made to determine the amounts of magnesium chloride and magnesium mixture necessary to keep certain amounts of pyrophosphate in solution. Then determinations were made to see if orthophosphate could be precipitated quantitatively from the magnesium chloride mixture solutions containing certain amounts of dissolved pyrophosphate.

TABLE I.

Separation of Orthophosphate from Pyrophosphate

Mgs. P used in form of ortho.	Mgs. P found in form of ortho.	Mgs. P used in form of pyro.	Mgs. P used in form of ortho.	Mgs. P found in form of ortho.	Mgs. P used in form of pyro.
30.60	30.38	40.	45.00	45.74	20.
30.53	30.38	40.	45.00	45.91	20.
30.53	30.16	40.	45.00	45.55	30.
30.53	30.75	40.	45.00	45.52	30.
30.53	30.58	30.	45.00	45.29	30.
30.53	30.30	30.	45.00	46.13	30.
30.53	30.61	30.	45.00	45.77	20.
30.53	30.53	20.	45.00	45.91	20.
30.53	30.38	20.	45.00	44.83	none
45.00	45.20	30.	45.00	44.74	none
45.00	44.83	none	45.00	46.41	30.
45.00	44.52	none	45.00	45.88	30.
44.90	45.69	30.	21.60	21.74	30.
45.00	46.41	30	21.60	21.49	30.
45.00	45.88	30.			

In Table 1 it is shown that from 30 to 45 milligrams of phosphorus as orthophosphate can be determined within two per cent. in the presence of 40 milligrams or less of phosphorus as pyrophosphate. Attempts to determine orthophosphate in greater concentrations of pyrophosphate were not successful because of the large amounts of the magnesium chloride mixture necessary to keep the pyrophosphate in solution which made the method cumbersome and inaccurate.

The following method for separation was developed: 170 c.c. of magnesium mixture and 85 c.c. of magnesium chloride solution (described under preparation of materials) were mixed just before using. This mixture of the two solutions has been called throughout this article "the magnesium chloride mixture." The pyrophosphate was dissolved in a few c.c. of water and added slowly with continuous stirring to the magnesium chloride mixture and stirred until any precipitate which formed was re-dissolved. The orthophosphate solution was added slowly with continuous stirring from a burette. The solution was then stirred until the precipitate became crystalline. It was then allowed to stand from twelve to fourteen hours, then filtered and washed with an ammonium nitrate and ammonium hydroxide solution. This precipitate was then dissolved in cold six molar hydrochloric acid and re-precipitated by adding twenty c.c. of 15 M. ammonium hydroxide and a few c.c. of magnesium mixture; stirring well during precipitation. It was allowed to stand from six to twelve hours, then filtered into a Gooch crucible and ignited and weighed as magnesium pyrophosphate.

By this method it was possible to precipitate the orthophosphate in a crystalline form. In most cases however, the first precipitate showed traces of pyrophosphate which forms a gelatinous precipitate with magnesium mixture. To minimize as much as possible hydrating this pyrophosphate to the orthophosphate during the dissolving of the precipitate with acid, cold acid was used and the solution run directly into the ammonium hydroxide used for re-precipitation. In spite of these precautions a small amount of pyrophosphate was hydrated during the operation as may be seen in Table 1, where a majority of the values show a slight increase in orthophosphate over that taken in the sample.

This method of separation can be used where the concentration of phosphorus as pyrophosphate does not exceed about 45 milligrams and the concentration of phosphorus as orthophosphate is about 30 to 45 milligrams in the total volume of 160 c.c. used. The limits of this method allow its use then only after the pyrophosphate solutions are over fifty per cent. hydrated and it was therefore used to check the values ob-

tained by hydrogen ion measurements over the last fifty per cent.

The method of sampling and analyzing the solutions being hydrated was as follows:

The concentration of the hydrogen ion was measured as described under measurement of hydrogen ion concentration at intervals of about every eight to ten per cent hydration. After the solutions were over fifty per cent hydrated gravimetric samples were taken at the same time as the hydrogen ion concentration samples. These samples were taken by means of a Bailey weighing burette. An effort was made to get samples in which the phosphorus as orthophosphate was within 30 to 45 milligrams. The sample was added drop by drop with constant stirring to the magnesium chloride mixture. When these samples containing both ortho and pyrophosphate were added a curdy precipitate of ortho with some pyrophosphate was formed. In order to re-dissolve the pyrophosphate it was necessary to stir for some time until the precipitate became distinctly crystalline and no curdy precipitate could be observed. The lengths of time to accomplish this varied, but thirty minutes was usually sufficient.

In this way two values were obtained for the percentage of hydration over the last fifty per cent. By referring to the tables under experimental data it may be seen that the first gravimetric samples gave values which were usually three to five per cent. higher than those obtained by hydrogen ion concentration measurements, and as the hydration neared completion and the concentration of pyrophosphate became less the agreement between the two values became better and near completion checked within the experimental limits. The reason for the greater deviation at first is due to the pyrophosphate carried down in the first precipitation which was partly hydrated on dissolving in acid for the second precipitation. It was found more difficult to re-dissolve the pyrophosphate in these samples than it was when it was added alone as was done in the development of the separation, and with the utmost precaution the first precipitates when filtered always showed the presence of a little pyrophosphate. Then as the pyrophosphate concentration in the samples decreased the

amount carried down was much less and agreement was obtained in the values by both methods. So by use of this gravimetric method it was possible to have a check over the last fifty per cent. on the values obtained by the hydrogen ion concentration measurements.

It can be seen by a comparison of the tables that the hydrogen ion concentration in each solution approached a final value very nearly the same as the value obtained for the analytical curves where the final solution was made up of disodium, orthophosphate and hydrochloric acid. Every solution was left in the thermostat from two weeks to a month and the hydrogen ion concentration measured two or three times after the final value which is given in the tables was obtained, and in every case the hydrogen ion concentration remained constant which shows that equilibrium had been reached.

In determining orthophosphate by magnesium mixture it is usually difficult to get perfectly white ignited precipitates. Nearly all show black spots after they have been ignited to the magnesium pyrophosphate. It was thought this might be due partly to suspended organic matter in the reagents or from such material in the air getting into the precipitate before it was ignited. To see if extra precautions to avoid contamination of the precipitates in this way would decrease the black spots after ignition, all reagents used in the final precipitation and washing were filtered and the precipitate protected from dust and dirt from the air as much as possible. These precautions were taken throughout this work and the majority of the precipitates were white, showing no black spots.

EXPERIMENTAL DATA

In the following table are outlined the solutions of normal sodium pyrophosphate and hydrochloric acid studied in securing the data for the hydration and for the effect of hydrogen ion concentration upon the rate of the hydration.

TABLE 2.
Solutions Studied

Solution	Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ in moles per Liter at 20° C.	Concentration of HCl in moles per Liter at 20° C.	Specific Gravity at 20° C.
A ₁	.125	.350	1.029
A ₂	.125	.350	1.029
H ₁	.125	.425	1.030
H ₂	.125	.425	1.030
I ₁	.125	.500	1.031
I ₂	.125	.500	1.031
C ₁	.175	.350	1.041
C ₂	.175	.350	1.040
F ₁	.175	.425	1.041
F ₂	.175	.425	1.041
G ₁	.175	.500	1.043
G ₂	.175	.500	1.043
B ₁	.225	.350	1.052
B ₂	.225	.350	1.052
D ₁	.225	.425	1.054
D ₂	.225	.425	1.054
E ₁	.225	.500	1.056
E ₂	.225	.500	1.056

It may be observed in the above outline that all hydrations were run in duplicate. In every case the two checked within experimental error and therefore the data for only one is given.

All synthetic solutions for analytical curves are lettered the same as the respective solutions to be hydrated.

TABLE 3.
Data for Analytical Curve I in Plate I.
Concentration of HCl = .500 M. at 20° C.
Temperature = 45° C.
Barometric Pressure = 766.0 mm. at 19° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^2$
1	.125	.000	.2892	13.39
2	.100	.050	.2919	12.14
3	.075	.100	.2958	10.52
4	.050	.150	.2999	9.06
5	.025	.200	.3056	7.36
6	.000	.250	.3112	5.99

TABLE 4.

Data for Analytical Curve H in Plate I.
 Concentration of HCl = .425 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 758.0 mm. at 21.5° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.125	.000	.3080	67.4
2	.100	.050	.3137	54.7
3	.075	.100	.3211	41.8
4	.050	.150	.3278	32.6
5	.025	.200	.3322	27.7
6	.000	.250	.3379	22.6

TABLE 5.

Data for Analytical Curve A in Plate I.
 Concentration of HCl = .350 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 744.0 mm. at 21° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.125	.000	.3313	28.7
2	.100	.050	.3392	21.6
3	.075	.100	.3470	16.4
4	.050	.150	.3535	12.8
5	.025	.200	.3597	10.0
6	.000	.250	.3646	8.5

TABLE 6.

Data for Analytical Curve G in Plate II.
 Concentration of HCl = .500 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 764.0 mm. at 20.5° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.175	.000	.3201	43.3
2	.140	.070	.3285	31.8
3	.105	.140	.3367	23.6
4	.070	.210	.3445	17.7
5	.035	.280	.3509	14.0
6	.000	.350	.3565	11.4

TABLE 7.

Data for Analytical Curve F in Plate II.
 Concentration of HCl = .425 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 766.0 mm. at 19.5° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.175	.000	.3557	11.80
2	.140	.070	.3661	8.06
3	.105	.140	.3738	6.08
4	.070	.210	.3809	4.58
5	.035	.280	.3865	3.82
6	.000	.350	.3910	3.24

TABLE 8.

Data for Analytical Curve C in Plate II.
 Concentration of HCl = .350 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 759.0 mm. at 19.5° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.175	.000	.4961	69.6
2	.140	.070	.4966	61.3
3	.105	.140	.5038	52.5
4	.070	.210	.5086	44.1
5	.035	.280	.5149	35.0
6	.000	.350	.5235	25.5

TABLE 9.

Data for Analytical Curve E in Plate III.
 Concentration of HCl = .500 M. at 20° C.
 Temperature = 45° C.
 Barometric Pressure = 770.0 mm. at 18° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^3$
1	.225	.000	.3767	5.45
2	.180	.090	.3883	3.58
3	.135	.180	.3970	2.61
4	.090	.270	.4036	2.05
5	.045	.360	.4101	1.61
6	.000	.450	.4138	1.41

TABLE 10.

Data for Analytical Curve D in Plate III.

Concentration of HCl = .425 M. at 20° C.

Temperature = 45° C.

Barometric Pressure = 752.0 mm. at 19° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^6$
1	.225	.000	.5273	22.2
2	.180	.090	.5315	19.1
3	.135	.180	.5354	16.5
4	.090	.270	.5402	13.9
5	.045	.360	.5468	10.9
6	.000	.450	.5522	9.0

TABLE 11.

Data for Analytical Curve B in Plate III.

Concentration of HCl = .350 M. at 20° C.

Temperature = 45° C.

Barometric Pressure = 762.0 mm. at 19° C.

Solution	Molar Concentration of $\text{Na}_4\text{P}_2\text{O}_7$ at 20° C.	Molar Concentration of Na_2HPO_4 at 20° C.	Voltage E	Molar Concentration of Hydrogen Ion $\times 10^6$
1	.225	.000	.5742	4.10
2	.180	.090	.5775	3.55
3	.135	.180	.5818	3.04
4	.090	.270	.5857	2.63
5	.045	.360	.5887	2.36
6	.000	.450	.5903	2.22

TABLE 12.
Hydration in Solution I_1
Concentration of $Na_4P_2O_7 = .125$ M. at 20° C.
Concentration of $HCl = .500$ M. at 20° C.
Temperature $= 45^\circ$ C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion per Liter $\times 10^2$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Percentage hydrated as deter- mined by hydrogen ion meas- urements	Per- centage hydrated by as deter- mined gravimet- rically	Total phos- phorus taken in sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_x - t_1}$	$K = \frac{1}{(K_4 - x)(C - x_1)}$
1	.2893	13.35	759.0	22.5	1.031
2	.2916	12.27	5:00	759.0	22.5	16.6
3	.2929	11.70	12:40	767.0	21.0	24.000524	.004379
4	.2938	10.53	23:45	771.0	20.5	40.000762	.006715
5	.2979	9.75	34:20	767.0	20.0	49.600745	.006832
6	.2994	9.23	47:49	762.0	20.0	56.600663	.006269
7	.3009	8.74	58:13	758.0	20.0	62.8	66.03	38.80	25.62	.00659	.006435
8	.3026	8.21	78:20	758.0	19.5	70.0	73.52	32.76	24.08	1.031	.00605	.006170
9	.3045	7.66	102:55	761.0	19.5	77.2	79.66	38.53	30.6900575	.006140
10	.3076	6.84	154:00	762.0	20.0	88.4	89.27	34.79	31.0500575	.006753
11	.3086	6.59	202:10	765.0	20.0	91.6	93.51	34.58	32.3400506	.006157
12	.3107	6.10	250:00	757.0	22.5	98.6	96.17	30.50	29.61	1.031	.00730	.012592

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate IV.

TABLE 14.
Hydration in Solution H_2
Concentration of $Na_2P_2O_7 = 0.125$ M. at 20° C.
Concentration of $HCl = .425$ M. at 20° C.
Temperature $= 45^\circ$ C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion per Liter $\times 10^3$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Total phos- phorus sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_2 - t_1} \log \frac{C - x_1}{C - x}$
1	.3085	66.2	758.0	21.5	1.030
2	.3105	61.5	10:08	760.5	22.0	9.6
3	.3141	53.9	25:13	761.0	21.0	20.400367
4	.3155	51.1	33:28	758.0	21.0	24.200327
5	.3187	45.6	53:48	748.0	20.0	33.000298
6	.3212	41.6	72:07	754.5	20.0	40.200296
7	.3247	36.6	100:04	764.5	19.5	50.600292
8	.3266	34.1	130:00	759.0	21.0	56.4	1.030	.00264
9	.3294	30.8	173:16	754.0	22.0	65.800259
10	.3314	28.9	226:00	764.0	20.5	73.0	79.14	42.44	33.59	.00243
11	.3325	27.5	274:09	757.0	20.5	78.0	82.04	36.45	29.91	.00233
12	.3356	24.5	368:35	764.0	20.0	88.0	89.52	38.33	34.32	.00245
13	.3368	23.5	587:25	770.0	20.0	96.0	96.82	29.97	29.02	.00239
14	.3378	22.7	701:46	753.0	21.5	100.0	98.69	30.73	30.33

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate IV.

TABLE 16.

Hydration in Solution A₁
 Concentration of Na₄P₂O₇ = .125 M. at 20° C.
 Concentration of HCl = .350 M. at 20° C.
 Temperature = 45° C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion Moles per Liter × 10 ³	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Total phos- phorus sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_2 - t_1} \log \frac{C - x_1}{C - x}$
1	.3313	28.7	753.0	20.0	1.029
2	.3321	27.9	6:51	750.0	20.0	1.5
3	.3350	25.1	22:45	744.0	21.0	9.400228
4	.3401	20.8	53:14	751.5	20.0	22.400223
5	.3449	17.5	96:28	761.0	22.0	35.000160
6	.3479	15.7	152:46	763.0	21.0	42.800162
7	.3532	12.9	250:07	763.0	20.0	58.6	62.94	44.77	30.80	.00154
8	.3548	12.2	297:09	760.0	20.5	63.9	68.16	31.57	21.52	.00150
9	.3559	11.7	344:15	67.2	72.30	41.98	30.36	.00142
10	.3590	10.4	511:45	758.0	20.0	77.3	83.51	43.17	36.04	.00126
11	.3607	9.8	655:52	762.0	21.0	83.6	91.42	22.95	21.47	.00120
12	.3611	9.7	801:23	769.0	21.0	85.2	91.42	43.54	39.81	.00103
13	.3641	8.7	1181:46	98.0	97.84	48.50	47.45	.00141
14	.3643	8.6	1302:33	744.0	21.0	99.0	99.58	38.27	38.03	.00154

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate IV.

TABLE 18.

Hydration in Solution G_1
 Concentration of $\text{Na}_4\text{P}_2\text{O}_7 = .175 \text{ M. at } 20^\circ \text{ C.}$
 Concentration of $\text{HCl} = .500 \text{ M. at } 20^\circ \text{ C.}$
 Temperature $= 45^\circ \text{ C.}$

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion Moles per Liter $\times 10^3$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Per- centage hydrated by as deter- mined met- rically	Total phos- phorus taken in sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_x - t_1} \log \frac{C - x_1}{C - x}$
1	.3200	43.5	764.0	20.5	1.043
2	.3217	40.9	7:00	764.0	20.5	4.0
3	.3256	35.4	23:52	758.0	20.5	14.000283
4	.3310	29.1	51:55	767.0	21.0	26.600234
5	.3349	25.2	78:31	767.0	21.5	35.400241
6	.3383	22.2	119:27	759.0	19.0	44.000208
7	.3421	19.5	154:12	770.0	20.0	53.400213
8	.3440	18.1	201:00	774.0	19.0	59.4	61.33	46.36	28.4300193
9	.3466	16.4	269:53	753.0	21.5	67.2	69.65	49.71	34.63	1.043	.00177
10	.3497	14.7	368:19	765.0	22.0	76.4	77.82	52.80	41.0900169
11	.3517	13.6	488:30	83.0	84.68	33.54	28.4100156
12	.3531	12.9	632:35	744.0	20.5	88.6	92.09	37.91	41.1300148
13	.3543	12.4	824:48	756.0	23.0	92.0	95.54	31.98	30.5600132
14	.3554	11.9	1016:27	767.0	20.5	96.6	99.70	33.78	33.6800144
15	.3554	11.9	1160:23	742.0	19.0	96.6	100.50	30.82	30.99	1.043	.00126

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate V.

TABLE 20.
Hydration in Solution F_1
Concentration of $Na_4P_2O_7 = .175$ M. at 20° C.
Concentration of $HCl = .425$ M. at 20° C.
Temperature = 45° C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion Moles per Liter $\times 10^3$	Time hrs. min.	Baro- metric pres- sure in mm. at Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Per- centage hydrated as deter- mined gravimet- rically	Total phos- phor- us in sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_x - t_1} \log \frac{C - x_1}{C - x}$
1	.3555	11.87	760.0	19.0	1.041
2	.3583	10.72	21:18	758.0	19.0	5.6
3	.3640	8.70	67:55	770.0	17.0	16.800118
4	.3683	7.44	116:00	768.5	18.5	26.000112
5	.3709	6.76	168:00	763.0	18.0	32.200098
6	.3770	5.41	284:30	763.0	17.0	48.000099
7	.3805	4.76	413:30	750.0	20.0	58.6	62.72	39.96	1.041	.00093
8	.3838	4.22	581:30	70.0	74.64	71.3400089
9	.3860	3.89	773:52	774.0	20.5	78.6	83.17	44.8700086
10	.3872	3.72	941:35	770.0	19.0	83.4	87.60	33.2900082
11	.3891	3.47	1277:15	772.0	20.5	92.2	95.14	26.6900086
12	.3915	3.17	1493:38	750.5	21.5	100.0	99.64	40.09	1.041

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate V.

TABLE 23.
Hydration in Solution C_2
Concentration of $Na_4P_2O_7 = .175$ M. at 20° C.
Concentration of $HCl = .350$ M. at 20° C.
Temperature = 45° C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion per Liter $\times 10^6$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Per- centage hydrated by as deter- mined gravimet- rically	Total phos- phor- us in sample in mgs.	Phos- phorus found as ortho at 20° C.	Specific gravity	$K = \frac{1}{t_x - t_1}$ centage deviation from average K	$K = \frac{1}{(K_4 - x)(C - x_1)}$ log $\frac{(C - x)(K_4 - x_1)}{(K_4 - x)(C - x_1)}$
1	.4962	69.4	768.5	18.0	1.040
2	.4982	64.5	71:41	760.0	19.0	11.6
3	.5001	60.1	143:27	770.0	17.0	21.0000680	16.80
4	.5010	58.2	244:05	763.0	18.0	26.0000448	11.41
5	.5050	50.3	365:53	763.0	17.0	44.0000674	2.0
6	.5063	47.9	479:04	754.0	19.0	51.0000629	4.8
7	.5091	43.3	579:00	760.0	19.0	60.0000678	2.5
8	.5117	39.3	752:32	767.0	20.5	69.2	67.44	43.65	29.44000673	1.9
9	.5134	37.0	896:26	767.0	19.5	73.8	74.09	46.55	34.49	1.040	.000640	3.2
10	.5149	35.0	1063:54	745.0	22.0	78.4	79.87	47.44	37.88000617	6.7
11	.5186	30.6	1447:36	766.5	21.0	87.8	88.97	40.48	36.02000625	5.4
12	.5196	29.5	1712:00	774.0	19.0	91.0	92.98	42.01	39.06000605	8.4
13	.5212	27.8	2072:12	761.0	20.5	95.0	95.52	34.81	33.26000624	5.4
14	.5217	27.3	2383:47	767.0	21.0	97.0	98.64	30.69	30.27	1.041	.000636	..

* .000661

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate V.
* Average neglects first and last points and point (4) which is off curve.

TABLE 24.
Hydration in Solution E_1
Concentration of $\text{Na}_2\text{P}_2\text{O}_7 = .225 \text{ M. at } 20^\circ \text{ C.}$
Concentration of $\text{HCl} = .500 \text{ M. at } 20^\circ \text{ C.}$
Temperature $= 45^\circ \text{ C.}$

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion in Moles per Liter $\times 10^3$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Per- centage hydrated phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_x - t_1} \log \frac{C - x_1}{C - x}$
1	.3768	5.45	762.0	17.0	1.056
2	.3832	4.32	46:40	763.0	17.0	11.4
3	.3881	3.61	99:48	766.0	19.0	20.600108
4	.3919	3.14	166:18	754.0	19.0	29.000080
5	.3973	2.58	266:08	760.0	19.0	41.800083
6	.3985	2.47	334:13	768.0	19.0	45.200073
7	.4027	2.12	512:18	773.0	19.0	57.0	65.17	47.65	.00068
8	.4069	1.81	680:11	771.0	18.5	70.0	74.20	43.92	.00074
9	.4085	1.71	872:08	754.0	21.0	75.0	82.00	43.71	.00067
10	.4116	1.53	1395:14	774.0	19.0	90.0	94.70	38.09	.00070
11	.4122	1.49	1688:28	776.0	21.5	95.0	98.12	43.39	.00076

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate VI.

TABLE 26.
Hydration in Solution D₁
Concentration of Na₄P₂O₇ = .225 M. at 20° C.
Concentration of HCl = .425 M. at 20° C.
Temperature = 45° C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion in Moles per Liter × 10 ⁶	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated as deter- mined by hydrogen ion meas- urements	Total phos- phor- us in sample in mgs.	Phos- phorus found as ortho at 20° C.	Specific gravity	$K = \frac{t_x - t_1}{C - x_1}$	Per- centage deviation from average $\log \frac{(K_4 - x)(C - x_1)}{(C - x)(K_4 - x_1)}$	$K = \frac{(t_x - t_1)K_2}{(K_4 - x)(C - x_1)}$
1	.5272	22.3	756.0	20.5	1.054
2	.5278	21.8	47:00	744.0	20.0	3.0
3	.5311	19.3	149:30	774.5	18.0	19.6000795	..	79.39
4	.5321	18.6	216:03	767.0	18.0	24.4000647	22.8	49.23
5	.5342	17.3	336:33	758.0	19.5	33.4000564	7.0	39.97
6	.5366	15.8	485:17	763.0	18.0	43.0000527	0.0	36.12
7	.5387	14.6	657:10	766.0	19.0	51.8000498	5.5	33.98
8	.5404	13.8	801:10	750.0	20.0	60.0	66.45	71.96	47.92	.000510	3.2	35.22
9	.5424	12.8	944:15	758.0	20.0	66.2	70.68	46.59	33.01	.000522	1.0	35.83
10	.5442	12.0	1113:55	772.0	20.0	73.0	76.88	50.16	38.58	.000521	1.0	36.68
11	.5454	11.5	1281:25	763.0	20.0	77.8	80.61	38.59	31.11	.000519	1.1	38.32
12	.5473	10.7	1617:15	761.0	19.5	84.4	87.46	41.22	36.06	.000505	4.2	38.96
13	.5488	10.1	2121:20	761.0	22.5	89.0	93.27	39.13	35.99	.000456	5.5	46.95
14	.5494	10.0	2719:00	761.0	19.5	90.0	99.27	36.25	35.98	.000369	..	77.61
										*Av. .000527		

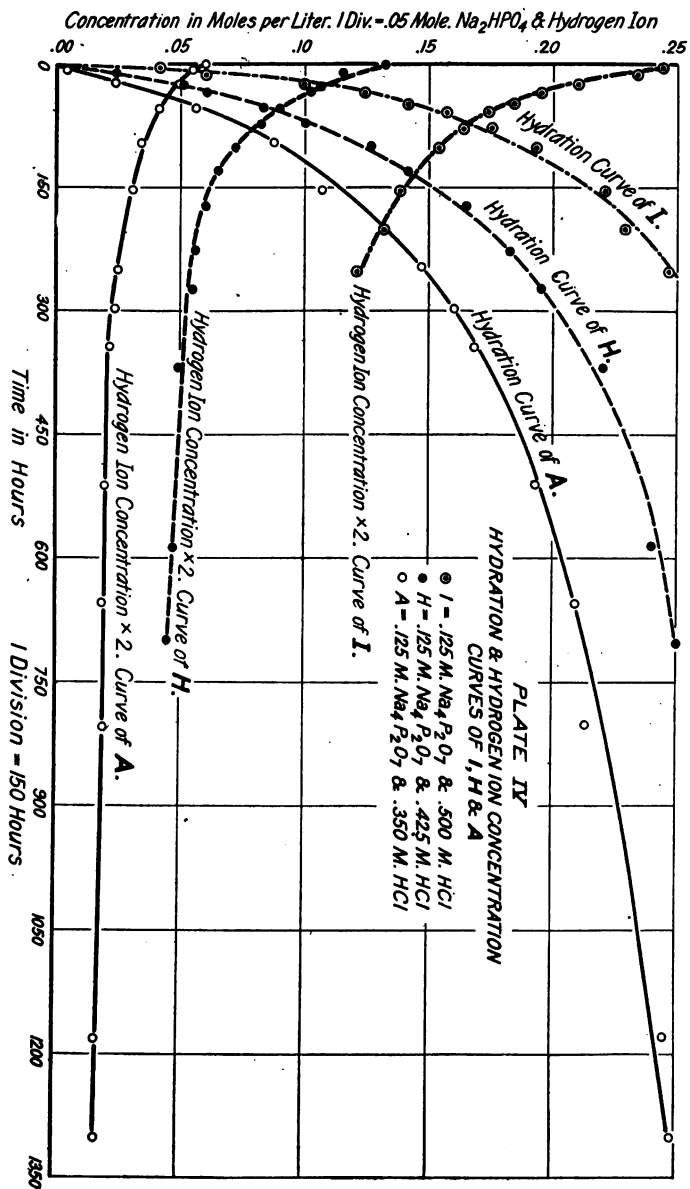
This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate VI.
* Average of K. neglecting first and last values.

TABLE 29.
Hydration in Solution B_2
Concentration of $Na_2P_2O_7 = 225$ M. at 20° C.
Concentration of $HCl = 350$ M. at 20° C.
Temperature $= 45^\circ$ C.

Sam- ple	Volt- age E	Concen- tration of Hydro- gen Ion in Moles per Liter $\times 10^3$	Time hrs. min.	Baro- metric pres- sure in mm. at	Temp. C.	Per- centage hydrated deter- mined by hydrogen ion meas- urements	Per- centage hydrated deter- mined by gravimet- rically	Total phos- phor- us in sample in mgs.	Phos- phorus found as ortho in mgs.	Specific gravity at 20° C.	$K = \frac{1}{t_x - t_1} \log \frac{C - x_1}{C - x}$
1	.5736	4.21	774.0	18.0	1.052
2	.5752	3.86	66:13	767.0	18.0	8.4
3	.5772	3.59	162:50	760.0	19.0	18.2000509
4	.5785	3.42	283:43	768.5	18.5	25.0000400
5	.5814	3.08	507:43	766.0	19.0	38.4000390
6	.5825	2.96	671:43	760.0	19.0	44.0000353
7	.5830	2.90	859:03	759.0	21.0	46.6000295
8	.5860	2.62	1296:09	764.5	19.5	61.4	63.08	48.35	30.50000308
9	.5875	2.46	1798:14	774.0	19.0	72.0	71.85	49.24	35.38000297
10	.5878	2.43	2284:05	759.0	21.5	75.8	80.74	39.71	32.06000261
11	.5889	2.34	2764:13	750.0	24.5	83.0	87.10	33.83	29.47	1.053	.000271

This table furnishes the data for the hydration and hydrogen ion concentration curves in Plate VI.

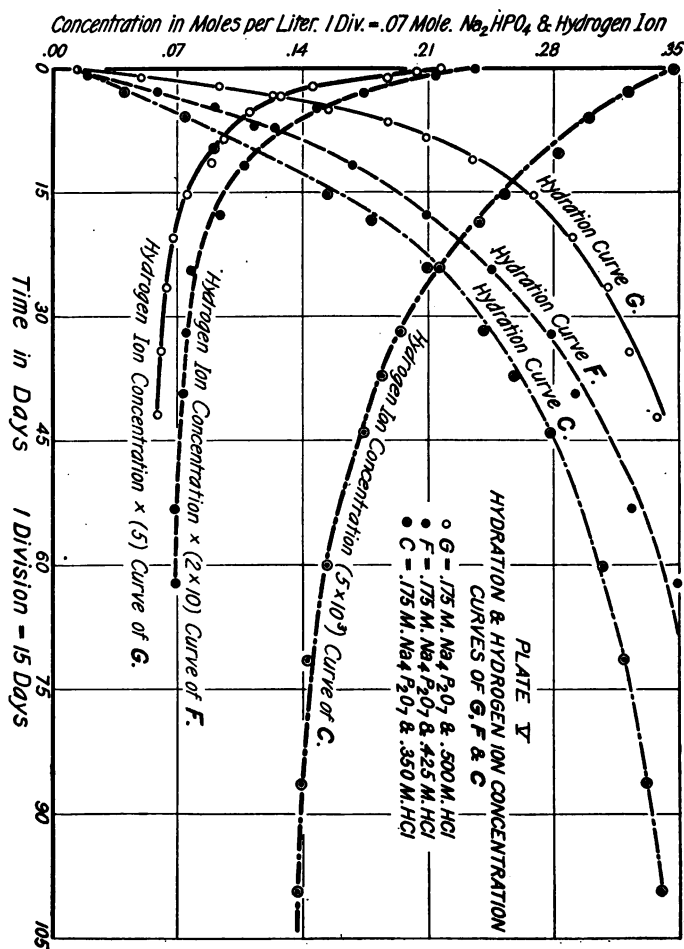
"Still in process of hydration but at present rate will require at least three months longer.



DISCUSSION

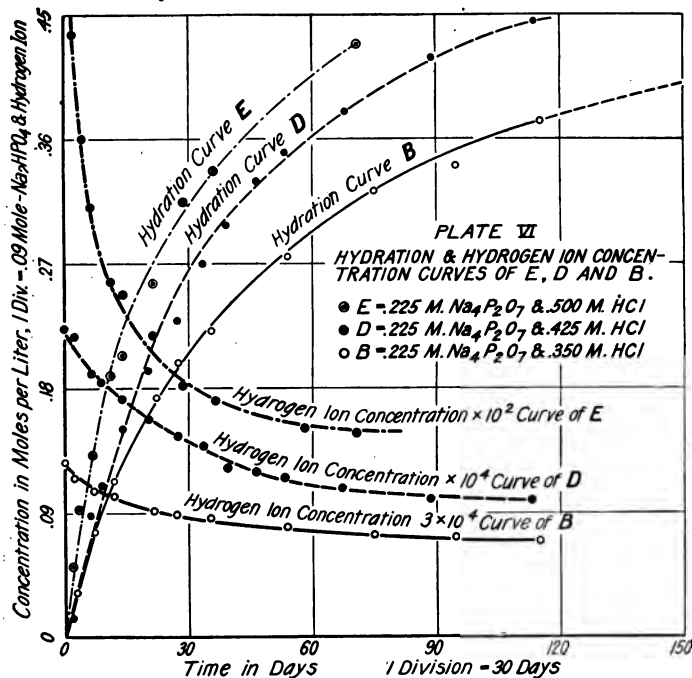
Change of Hydrogen Ion Concentration During Hydration.

By adding acid directly to the normal sodium pyrophosphate solutions it was possible to obtain any desired concentration of hydrogen ion and determine its influence. In order to show this influence the hydration curves of one concentration of normal sodium pyrophosphate in the three different acid concentrations used have been plotted on one plate. All hydration curves are plotted from the results obtained by



hydrogen ion concentration measurements except the last two points on curve D in which the hydrogen ion concentration measurements did not agree with the gravimetric determinations used.

On plate IV are plotted the hydration curves of .125 M. normal sodium pyrophosphate in .350 M., .425 M., and .500 M. hydrochloric acid, and on plates V and VI are plotted the hydration curves of .175 M. and .225 M. normal sodium pyrophosphate respectively in each of the three concentrations of acid. On the same plates are plotted the hydrogen ion concentration curves for each of the solutions. The hydrogen ion concentrations have been multiplied by values such that they could be plotted on the same concentration scale as the hydration curves, thus showing the relative decrease in hydrogen ion concentration as the hydration proceeded. From these hydrogen ion concentration curves in the three plates it is seen that in every solution there was a gradual decrease in hydrogen ion concentration as the hydration proceeded,—



finally reaching a constant value at completion. The gradual decrease of hydrogen ion concentration as the concentration of orthophosphate gradually increased is accounted for by the less dissociated orthophosphoric acid.

By referring to the tables of data for the analytical curves it is seen that in the same hydrochloric acid concentration an increase both of pyrophosphate and of orthophosphate causes a decrease in hydrogen ion concentration. So it was possible by the use of three concentrations of pyrophosphate and three concentrations of acid to have nine solutions of different hydrogen ion concentration and in that way to study the effect of the hydrogen ion concentration on the rate of hydration.

By a comparison of the hydration curves in the three plates, and of the data for these curves given in the tables for the different solutions it may be seen that the times required for equilibrium within experimental error for .125 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M., .425 M., and .350 M. HCl were respectively 250 hours, 702 hours, and 1,302 hours; for a .175 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M., .425 M., and .350 M. HCl the times for equilibrium were 1,160 hours, 1,493 hours and 2,386 hours respectively; and for a .225 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M. and .425 M. HCl the times for equilibrium were 1,688 hours and 2,719 hours respectively; and for .225 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .350 M. HCl, 2,766 hours were required for 81% hydration. If it continued at the rate at which it was going over the last 20 per cent., it would require at a minimum three months longer for completion.

From a comparison of the hydrogen ion concentrations in these solutions it is observed that the solutions of highest initial hydrogen ion concentration required the least time for equilibrium, the time increasing as the initial hydrogen ion concentration decreased. This was also shown in the hydration of sodium monometaphosphate⁸. These times show the great influence that hydrogen ion has upon this hydration.

Effect of Concentration of Pyrophosphate on the Rate of Hydration.

Abbott⁹ from his investigation of the hydration of pyrophosphoric acid calculated the rate of hydration (1) "on the

assumption that the rate of hydration is proportional both to the hydrogen ion concentration and to that of the pyrophosphoric acid undergoing hydration," and (2) "on the assumption that the rate is independent of the hydrogen ion concentration and is determined only by the concentration of the pyrophosphoric acid." The constants calculated on the second assumption were more nearly constant and he concludes from that, that the rate of hydration is approximately proportional to the concentration of pyrophosphoric acid present and that it increases with the concentration of hydrogen ion.

To see if the reaction studied in this investigation was of the first order and if constants calculated for a first order reaction would be of value in studying it, they have been calculated from the first determination for each solution

hydrated according to the formula $K = \frac{1}{t_x - t_1} \log \frac{C - x_1}{C - x}$, where

C is the original concentration of pyrophosphate and x the amount changed to orthophosphate in time t. This assumes then that the rate of hydration is a direct function of the concentration of pyrophosphate. These constants are given in the tables of data for each solution; they show a progressive decrease as the hydrogen ion concentration shows a progressive decrease from the solutions which have the lowest concentration of pyrophosphate and highest concentration of hydrogen ion down to the solutions having the highest concentration of pyrophosphate and lowest concentration of hydrogen ion, both in the individual solutions and among the solutions except in solutions C and D where they approach more nearly a constant value.

From this decrease in the constants it is evident that the rate of hydration of normal sodium pyrophosphate in the presence of hydrogen ion is not a direct function of the pyrophosphate concentration alone. It is increased by the hydrogen ion present and as the hydrogen ion concentration decreases the rate decreases.

In Table 23 for solution C₂ in which the ratio of pyrophosphate to hydrochloric acid is 1 mole to 2 moles, the con-

stants do not decrease regularly but tend to approach a constant. The mean value of these constants has been calculated and is given in the table. This mean neglects point four which is probably in error as shown by the hydration curve, and also the first and last values which are less accurate in most of the tables. In the last column of that table are the percentages of deviation of each of the constants from the mean. In this column it is shown that eight and four-tenths per cent. is the greatest deviation from the mean while most of the values are within four to five per cent. Constants were calculated for some of the value by using a value for the percentage hydrated at time t two per cent. greater than that determined and given in the table. It was found that this change of two per cent. caused an increase in the value of the constant from five to ten per cent., depending on what part of the curve the value was selected.

While it may seem that values for the constants in solution C_2 are tending to approach a constant within experimental error, they are, however, still tending to show a very small decrease. It does not seem then that the rate of hydration in this solution can be said to be directly proportional to the pyrophosphate concentration but to approach it very closely.

In Table 26 for solution D where the ratio of pyrophosphate to acid is 1 mole to 1.888 moles, the constants are also quite constant. The mean value and percentage deviations from it have been calculated and are given in the table as described above for solution C. The error caused by two per cent. change in percentages hydrated is from five to ten per cent. in this solution as in solution C. It is seen that in this solution the constants are also tending to approach a constant value within experimental error but as in solution C the constants are tending to show a small decrease so that the rate of hydration in this solution also is not quite a direct function of the pyrophosphate concentration alone but is approaching it.

Since the constants for solutions C and D where the ratio of pyrophosphate to acid is about 1 mole to 2 moles are very nearly constant and in all other solutions the constants show

a gradual decrease, it seems that two influences must be active in this hydration. Any discussion of the mechanism of the reaction is necessarily limited by the lack of the ionization constants of pyrophosphoric and orthophosphoric acids at this temperature and by the lack of a method for determining the concentration of any of the respective pyro and orthophosphate ions. The results show that hydrogen ion has a marked influence on the rate of hydration and as the concentration of hydrogen ion decreases the rate also decreases. Therefore if the hydrogen ion was the only factor in this hydration, the constants as calculated should show a progressive decrease as the hydrogen ion concentration shows a progressive decrease. Since the constants do not show this decrease in solutions C and D, some influence must be at work in the reaction to balance the decreasing influence of the hydrogen ion.

In this investigation where the concentration of hydrogen ion was not sufficient in most of the solutions to form very much pyrophosphoric acid it seems that the active component undergoing hydration must be one of the ionic products of pyrophosphoric acid, as the pyrophosphoric acid would decrease as the hydrogen ion concentration decreased. If, then, the active component undergoing hydration is one of the ions, the rate of hydration would therefore depend in part on the concentration of that ion. It then follows that hydrogen ion should show a slight negative influence on this hydration due to repression of the active ion. The negative influence of hydrogen ion must be very slight compared to the positive influence because the results show the higher the concentration of hydrogen ion the greater is the rate of hydration. It seems not impossible, however, that an initial concentration of hydrogen ion and of pyrophosphate might be obtained in which the removal of a very small amount of hydrogen ion would result in the formation of a much larger concentration of this active ion undergoing the hydration and therefore as the influence of the hydrogen ion on the hydration decreased the effect of the active ion would increase and the two balance each other. This seems to be the case in solu-

tions D and C where the constants obtained for a first order reaction show a very slight decrease in their values.

The curves obtained by plotting molar concentration of pyrophosphate against molar concentration of hydrogen ion are straight lines or very nearly so for solutions C, D, and I. Therefore the hydrogen ion concentration in these solutions is apparently directly proportional to the pyrophosphate concentration as the hydration proceeds. Similar curves for the other solutions are not straight lines but show decreasing slopes as the pyrophosphate concentration decreases. Since the orthophosphoric acid ions H_2PO_4^- and HPO_4^{2-} are much less dissociated than the respective pyrophosphoric acid ions $\text{H}_2\text{P}_2\text{O}_7^-$ and $\text{HP}_2\text{O}_7^{2-}$, it follows that in order for the pyrophosphate concentration to show a constant ratio to the hydrogen ion concentration that the pyrophosphoric acid ions must maintain a sufficient concentration of hydrogen ion through dissociation to keep the ratio constant, as the hydrogen ion concentration is being decreased in forming the less dissociated orthophosphoric acid ions. Therefore the rate of dissociation of the pyrophosphoric acid ions must continually increase as the orthophosphate is formed.

If as postulated the active principle undergoing hydration is one of the ions of pyrophosphoric acid it is evident then that its positive influence would increase as the hydration proceeded and this influence might approach a value sufficient to counterbalance the decreasing influence of hydrogen ion upon the hydration and therefore give a constant value for the constants as calculated for a first order reaction. From the greater influence which hydrogen ion has upon the reaction, its decrease could only be counterbalanced by the positive influence of pyrophosphate concentrations in solutions in which the initial hydrogen ion concentration was relatively small as in solution D where it was 22.1×10^{-6} moles per liter and in solution C where it was 69.4×10^{-6} moles per liter. Whereas in solution I where the initial hydrogen ion concentration was 13.4×10^{-2} moles per liter and the ratio of acid was four moles to one mole of pyrophosphate, the curve is a straight line but the constants show a progressive decrease. This seems to point to the conclusion that one of the

lower acid ions of pyrophosphoric acid or the pyrophosphate ion is the active component undergoing hydration and that the influence of its concentration is very small compared to the influence of hydrogen ion. It appears, therefore, that in the higher concentrations of hydrogen ion the formation of the active ion undergoing hydration is not sufficient to counterbalance the decreasing influence of the hydrogen ion concentration and accordingly the constants calculated show a progressive decrease.

In solution B, however, the ratio of acid to pyrophosphate was 1.555 moles to 1 mole and the initial hydrogen ion concentration was 4.1×10^{-6} moles per liter. So the influence of the hydrogen ion upon the repression of the active ion is less at the start than in solutions C and D. Therefore as the hydrogen ion concentration decreases and its influence decreases it is not balanced by the formation of an appreciably greater concentration of the active ion. Accordingly in this solution the constants show a progressive decrease.

In the foregoing discussion of the hydration in solutions C, D, and I, it was pointed out that the concentration of hydrogen ion was directly proportional to the pyrophosphate concentration. Therefore it is possible to express the concentration of hydrogen ion in terms of pyrophosphate concentration. By doing this and by assuming that the rate of hydration is a direct function of both the pyrophosphate concentration and the hydrogen ion concentration it is possible to formulate an expression which would give the influence of the changing hydrogen ion concentration at any instant in the hydration.

With this assumption the following development is made:

$$\frac{dx}{dt} = K_1(c-x)C_{H^+}$$

c = molar concentration of pyrophosphate.

x = amount of pyrophosphate changed in any time t .

$$C_{H^+} = a(c-x) + K_2$$

a = the slope of the line.

K_2 = hydrogen ion concentration at complete hydration.

This equation represents the concentration of hydrogen ion at any time t .

$$\therefore \frac{dx}{dt} = K_1(c-x)(a(c-x)+K_2)$$

The integration of the above expression between the limits t_1 and t_x gives the following formula:

$$K_1 = \frac{1}{(t_x - t_1)K_2} \log \frac{(K_4 - X)(c - x_1)}{(c - x)(K_4 - X_1)}$$

$$K_4 = \frac{ac + K_2}{a}$$

Using this formula constants have been calculated for solutions I_1 , C_2 , and D_1 . They are given in the last column of Tables 12, 23, and 26 respectively.

In Solution I_1 the concentration of pyrophosphate was .125 M. and the concentration of hydrochloric acid was .500 M. The change of hydrogen ion concentration was from 13.35×10^{-2} to 6.10×10^{-2} moles per liter. The constants calculated by this formula show a slight tendency to decrease as they do when calculated on the assumption that the rate of hydration is directly proportional to the pyrophosphate concentration alone.

In solution C_2 the constants show a progressive increase. In this solution the concentration of pyrophosphate was .175 M. and the hydrochloric acid was .350 M. The change of hydrogen ion concentration was from 69.4×10^{-6} to 27.3×10^{-6} moles per liter.

In solution D_1 the constants decrease to a minimum and then increase to their former values. In this solution the concentration of pyrophosphate was .225 M. and the concentration of hydrochloric acid was .425 M. The change of hydrogen ion concentration was from 22.3×10^{-6} to 10.0×10^{-6} moles per liter.

In solution I_1 the concentration of pyrophosphate was low and the hydrogen ion concentration was high. In solution D_1 the pyrophosphate concentration was high and the hydrogen ion concentration was low. In solution C_2 the pyrophosphate concentration was between that of solutions I_2 and D_1 , and the hydrogen ion concentration was a little greater than that of D_1 . The constants for solution I_1 by both formulas

show about the same decrease. In solutions C_2 and D_1 , by the first formula the constants approach quite closely a constant value. By the second formula in solution C_2 they show a progressive increase. In solution D_1 they pass through a minimum.

From this study then the results seem to point to the conclusion that one of the ionic products of pyrophosphoric acid, possibly the pyrophosphate ion, is the active component undergoing hydration and that hydrogen ion shows a slight negative influence due to the repression of this active component but this negative influence is only very slight compared to the positive influence shown by the hydrogen ion. Therefore, the rate of hydration of sodium pyrophosphate is not a direct function of the pyrophosphate concentration nor of the hydrogen ion concentration, due to the three influences that hydrogen ion must have in the hydration;—first of repression of the pyrophosphoric acid ionization, second of repression of the orthophosphoric acid ionization, and third, and by far the greatest, that of increasing the rate of the hydration.

The curves appearing in this article were prepared from tracing made by Mr. S. J. Ballard, draftsman, of the Department of Chemical Engineering.

SUMMARY

I. Three concentrations of Normal Sodium Pyrophosphate each in three different concentrations of hydrochloric acid, making nine solutions of different hydrogen ion concentration were studied.

II. By use of analytical curves obtained by making up synthetic solutions and plotting molar concentration of hydrogen ion against molar concentration of di-sodium orthophosphate, each hydration was followed to completion by hydrogen ion concentration measurements.

III. The last fifty per cent. of each hydration was checked by the standard gravimetric method. The separation of

ortho- and pyrophosphate was made by use of a magnesium chloride mixture.

IV. The hydrogen ion concentration in each solution decreased progressively with time reaching a final constant value.

V. The times required for equilibrium within experimental error for a .125 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M., .425 M., and .350 M. HCl were 250 hours, 702 hours, and 1,302 hours respectively; for a .175 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M., .425 M., and .350 M. HCl the times for equilibrium were 1,160 hours, 1,493 hours, and 2,386 hours respectively; and for a .225 M. $\text{Na}_4\text{P}_2\text{O}_7$ solution with .500 M. and .425 M. HCl the times for equilibrium were 1,688 hours and 2,719 hours respectively. 2,766 hours were required for 81% hydration of a .225 M $\text{Na}_4\text{P}_2\text{O}_7$ solution with .350 M. HCl. It would require at a minimum three months longer for completion if it continued at the same rate as it was going over the last twenty per cent.

VI. The influence of hydrogen ion cannot be accounted for by its effect upon the ionic equilibrium of the pyrophosphoric and orthophosphoric acid alone.

REFERENCES

- ¹ Graham, Phil. Trans., 123, 53, 1833.
- ² Sabatier, Compt. Rendu., 106, 63, 1888.
- ³ Montemartini and Egid, Gass. Ital. Chim., 31 I, 394, 1901.
- ⁴ Balareff, Zeit. Anorg. Chem., 67, 234, 1909; 68, 288, 1901; 96, 103, 1916.
- ⁵ Berthelot and André, Compt. Rendu., 123, 776, 1896; 124, 265, 1897; 124, 261, 1897.
- ⁶ Giran, J. Russ. Chem. Soc., 30, 99.
- ⁷ Holt and Meyers, J. C. S. Trans., 99, 385, 1911.
- ⁸ Beans and Kiehl, Unpublished work. (Submitted as Dissertation by Kiehl, 1921).
- ⁹ Abbott, J. A. C. S., 31, 763, 1909.
- ¹⁰ Fales and Vosburg, J. A. C. S., 40, 1291, 1918.
- ¹¹ Ellis, J. A. C. S., 38, 737, 1916.
- ¹² Hulett, Zeit. Physik. Chem., 33, 611, 1920.
- ¹³ Fales and Mudge, J. A. C. S., 42, 2434, 1920.
- ¹⁴ Arnold and Werner, Chem. Zeit., 29, 1905.

VITA

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